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Li, Jun; Gottardi, Stefano; Solianyk, Leonid; Moreno Lopez, Juan Carlos; Stöhr, Meike

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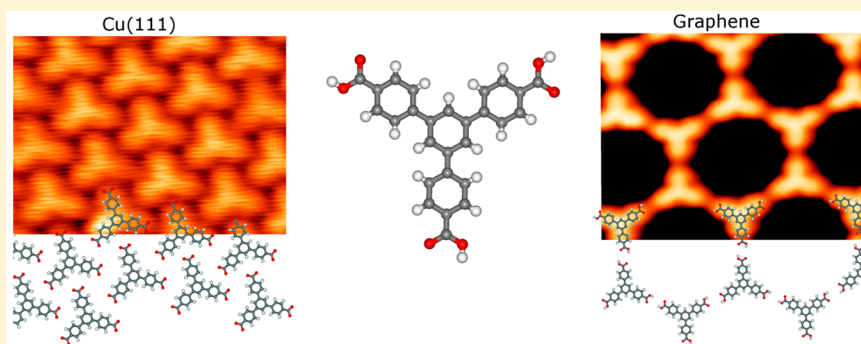
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1,3,5-Benzenetribenzoic Acid on Cu(111) and Graphene/Cu(111): A Comparative STM Study

Jun Li, Stefano Gottardi, Leonid Solianyk, Juan Carlos Moreno-López, and Meike Stöhr*

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

S Supporting Information



ABSTRACT: The self-assembly of 1,3,5-benzenetribenzoic acid (BTB) molecules on both Cu(111) and epitaxial graphene grown on Cu(111) were studied by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) under ultrahigh vacuum conditions. On Cu(111), the BTB molecules were found to mainly arrange in close-packed structures through H-bonding between the (partially) deprotonated carboxylic acid groups. In addition, porous structures formed by intact BTB molecules and also based on H-bonding were observed. On graphene grown on Cu(111) the BTB molecules mainly form porous structures accompanied by small patches of disordered close-packed structures. Upon annealing, BTB adsorbed on Cu(111) is fully deprotonated and arranges in the close-packed structure while in contrast on graphene/Cu(111) the porous network is exclusively formed. This shows that the molecular self-assembly behavior is highly dependent on the first substrate layer: one graphene layer is sufficient to considerably alter the interplay of molecule substrate and intermolecular interactions in favor of the latter interactions.

INTRODUCTION

Graphene is considered as a wonder material due to its countless outstanding properties,^{1,2} which make it the candidate of choice for numerous applications in areas ranging from photovoltaics over sensing to electronics.^{3–6} Because of its two-dimensional structure, graphene generally will be in touch with other materials. For example, in the field of graphene-based organic electronics, the interaction between organic molecules and graphene is expected to play an important role in the performance of these devices.^{7–9} Therefore, an improved understanding of the self-assembly of molecules on graphene becomes of vital interest, also in view of industrial applications. So far, experimental investigations of molecular self-assembly on graphene have been mainly focused on commercially available molecules like perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA),¹⁰ perylene tetracarboxylic diimide (PTCDI),¹¹ pentacene,¹² and further other molecules.^{13–16} There have been also a number of theoretical studies reported which often focus on the changes in the band structure of graphene due to the adsorption of organic molecules with the goal to identify a molecule which leads to the opening of a band gap at the K point.^{17–19} On the other hand, graphene is in contact with a support layer, on which it

either has been grown via chemical vapor deposition (CVD) or placed via a transfer technique. Because of the single-atom-thickness of graphene, adsorbed molecules will likely “feel” the underlying substrate and thus, the molecular layer formation as well as the electronic properties will depend on both the interaction with graphene and the underlying substrate. For example for graphene on Ru(0001), the adsorption of C₆₀²⁰ and Fe phthalocyanine²¹ as well as tetracyanoquinodimethane (TCNQ)²² were found to be guided by the Moiré pattern which graphene exhibits on Ru(0001). Moreover, for TCNQ on graphene/Ru(0001) magnetic properties were found for the originally nonmagnetic TCNQ molecules arising due to the influence of the Ru substrate. Therefore, a comparative study of the molecular adsorption behavior on graphene as well as on the supporting substrate of graphene will shed light on the molecule/graphene interface properties.

In this article, we present a comparative study of the self-assembly behavior of 1,3,5-benzenetribenzoic acid (BTB) on graphene grown on Cu(111) and of BTB on bare Cu(111).

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Scanning tunneling microscopy (STM) measurements showed that for BTB deposited on Cu(111) held at room temperature hexagonal porous structures of small sizes coexist with close-packed structures. While the molecules in the porous structures are intact the ones in the close-packed structure have their carboxylic acid groups deprotonated. Upon annealing at elevated temperatures, all BTB molecules get deprotonated and only the close-packed structure forms. On the other hand, when BTB is deposited on graphene the molecules are mainly found to form the hexagonal porous network already observed on Cu(111). Improved quality and increased size of the porous network domains are achieved upon annealing at 365 K. Low energy electron diffraction (LEED) measurements suggest that the porous network preferably aligns along principal directions of the graphene lattice.

EXPERIMENTAL METHODS

Structural Characterization. The STM measurements were performed at 77 K under ultrahigh vacuum conditions (base pressure $\sim 10^{-11}$ mbar) with a commercial low temperature STM (Scienta Omicron GmbH). The STM tip was made from a mechanically cut Pt/Ir wire. All bias voltages are given with respect to a grounded tip. The STM images were acquired in constant current mode and were analyzed with the WSxM software.²³ LEED measurements were performed at room temperature.

Graphene Preparation. The Cu(111) surface was first cleaned by repeated cycles of Ar⁺ sputtering (5.0 Messer) and annealing (800 K) in ultrahigh vacuum and then transferred to an ex-situ oven for the graphene growth. Graphene was grown by cracking methane on the Cu(111) surface at around 1270 K. A detailed description can be found in ref 24. After graphene was grown on Cu(111), the samples were transferred back to the UHV system where they were degassed at 700 K for 30 min to remove residual water and further adsorbates that might adsorbed onto graphene during the short transfer of the sample through air.

Molecule Deposition. BTB with a purity of 98% was purchased from Sigma-Aldrich. The structure of BTB is shown in Figure 1. Deposition of BTB was done *in situ* from a commercial molecule evaporator (OmniVac) onto the sample kept at room temperature. Before depositing the molecules onto Cu(111) and graphene, the BTB molecules were thoroughly degassed.

RESULTS AND DISCUSSION

As shown in Figure 1, each BTB molecule has three carboxylic acid groups forming an angle of 120° with respect to each other. The carboxylic acid groups can serve as both donor and acceptor for hydrogen bonds. Therefore, BTB molecules are good candidates for the formation of H-bonded porous networks. So far, the adsorption behavior of BTB has been investigated on Ag(111) under UHV conditions²⁵ and on HOPG at the solid-liquid interface.^{26–28} For both substrates a hexagonal porous network has been observed. On Ag(111), in dependence of the annealing temperature, two other more densely packed structures have been observed which are based on the interaction of partially deprotonated BTB molecules. On HOPG a so-called oblique structure exhibiting a denser packing than the porous network has been found. In our study, the BTB molecules formed two different assembly structures upon deposition on Cu(111) held at room temperature (Figure 2a).

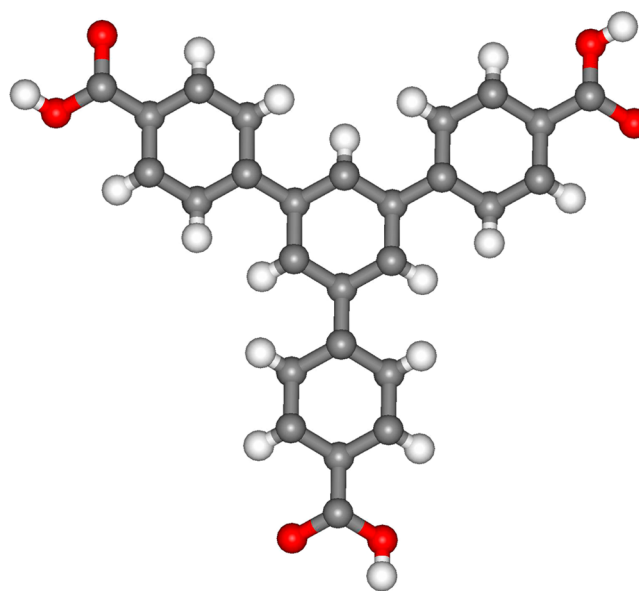


Figure 1. Structure of 1,3,5-benzenetribenzoic acid. Carbon atoms are gray, oxygen atoms red, and hydrogen atoms white.

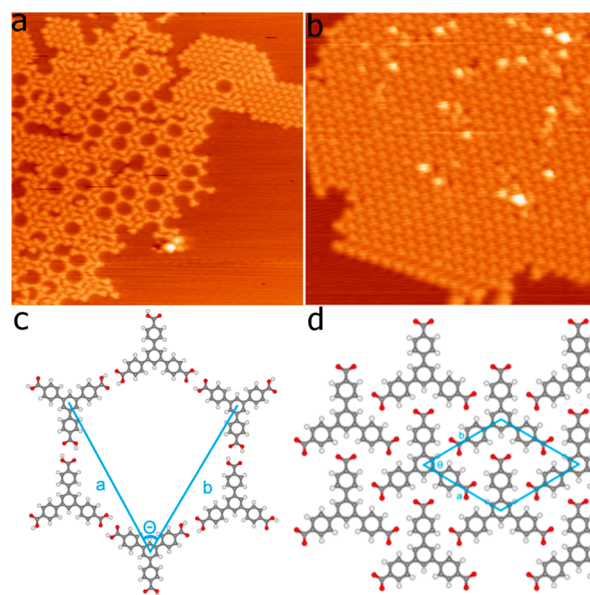


Figure 2. (a) STM image (47 nm \times 47 nm, $U = -1.5$ V, $I = 20$ pA) for BTB deposited on Cu(111) held at room temperature. The molecules arrange in a close-packed structure as well as a porous network. Both structures coexist on the surface. (b) STM image (32 nm \times 32 nm, $U = -1$ V, $I = 20$ pA) after annealing the sample at 385 K. Now, only the close-packed structure is observed. (c) Tentative structural model of the porous network formed by double hydrogen bonding between neighboring molecules. The unit cell is marked in blue. (d) Tentative structural model of the close-packed pattern formed by deprotonated BTB molecules. The unit cell is marked in blue.

A hexagonal porous network and a close-packed structure were found to coexist. The BTB molecules in the hexagonal porous network interact via double hydrogen bonding between their carboxylic acid end groups similar to what has been observed on Ag(111) and HOPG.^{25,26} In Figure 2c, the tentative structure model for a pore consisting of six BTB molecules is displayed. The unit cell of the porous network was measured to be $a = b = 3.2 \pm 0.2$ nm, with an angle $\theta = 60 \pm 1^\circ$. Besides the

porous network, a close-packed structure was also observed. The BTB molecules are oriented in the same direction and the carboxylic acid groups point to the center of neighboring BTB molecules. The unit cell of the close-packed structure was measured to be $a = b = 1.24 \pm 0.11$ nm with an angle $\theta = 60 \pm 1^\circ$. When building the structure model, it turns out that the hydrogen atoms of the hydroxyl groups are too close to the hydrogen atoms of the CH groups of neighboring BTB molecules. This would result in repulsive interactions and prevent the formation of a stable structure. Studies on related molecules having carboxylic acid end groups showed that the hydroxyl groups get deprotonated upon deposition on Cu surfaces.^{29–32} Therefore, we suggest that the BTB molecules in the close-packed structure are deprotonated. The deprotonated carboxylic acid groups point to the center of neighboring BTB molecules and two hydrogen bonds are formed between the oxygen atoms of the COO group and hydrogen atoms of neighboring CH groups (see structure model in Figure 2d). A close inspection of the STM images revealed that some of the BTB molecules are partially deprotonated (see Supporting Information). Figure 2b displays an STM image taken for a sample which was annealed at 385 K. The porous network structure disappeared and only the same close-packed structure already observed for room temperature preparation is present. It can be concluded, in accordance with what is reported for related molecules,^{29–32} that the deprotonation process is enhanced upon annealing. For annealing BTB on Cu(111) at 385 K all molecules are deprotonated and thus, the close-packed structure is the only structure present after annealing.

In a next step the influence of a graphene layer adsorbed on the Cu(111) surface on the adsorption behavior of BTB was investigated and the findings are compared to BTB on Cu(111). Graphene was grown on Cu(111) according to the procedure described in ref 24. The pristine graphene sample was first checked by LEED and STM before depositing BTB onto it. Figure 3a shows the LEED pattern of graphene grown

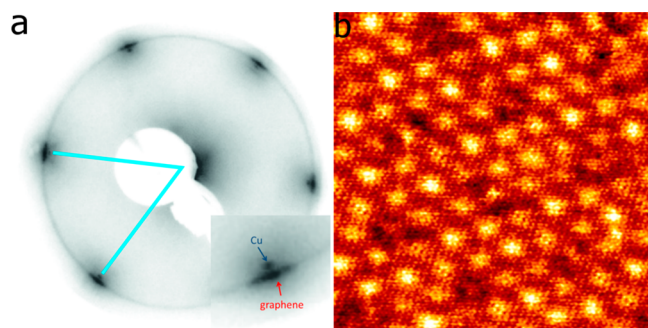


Figure 3. (a) LEED pattern of graphene grown on Cu(111) taken at an energy of 74.5 eV. The light blue lines indicate the Cu directions. In the inset, the diffraction features originating from Cu and graphene are marked by a blue and red arrow, respectively. (b) STM image (18 nm \times 18 nm, $U = -1.5$ V, $I = 10$ pA) showing the Moiré pattern as well as atomic resolution of graphene on Cu(111).

on Cu(111) taken at an energy of 74.5 eV. The Cu(111) reciprocal unit cell vectors are marked in blue. The ring around the first order Cu(111) diffraction spots indicates both the successful synthesis of graphene and its polycrystallinity. The ring exhibits increased intensity in the vicinity of the first order Cu(111) diffraction spots, suggesting a preferred orientation of graphene with respect to the Cu lattice.^{33,34} Figure 3b shows an

STM image for graphene on Cu(111). Atomic resolution as well as a Moiré pattern originating from the lattice mismatch between graphene and the underlying Cu(111) surface can be observed.³⁵ Depending on the specific angles between the principal directions of graphene and the Cu(111) surface, a number of different periodicities for the Moiré patterns can be observed.^{36–38}

After the deposition of BTB onto graphene/Cu(111) held at room temperature, the sample was cooled down to 77 K for STM measurements. In Figure 4a, a representative STM image is displayed. The BTB molecules tend to arrange in a hexagonal porous network, while to a smaller extent a close-packed and disordered arrangement is also observed. Annealing the sample at 365 K resulted in the (almost) exclusive formation of the hexagonal porous network (Figure 4b). Compared to the not annealed sample the average island size considerably increased, now exhibiting long-range order. The high resolution STM image in Figure 4c reveals the detailed structural arrangement of BTB on graphene/Cu(111). The arrangement in a honeycomb structure is similar to what was observed on the Cu(111) surface (Figure 2c). Each pore consists of six BTB molecules and each BTB molecule interacts with three neighboring BTB molecules via double hydrogen bonding. The unit cell is rhombic and marked in blue in Figure 4c. The lattice parameters determined from the STM data are $a = b = 3.27 \pm 0.15$ nm and the angle $\theta = 60 \pm 1^\circ$ and each unit cell contains two BTB molecules. Annealing at 365 K promoted the formation of molecular islands with a larger size and long-range order. Thus, it can be concluded that the mobility of the BTB molecules on the graphene surface increased upon annealing resulting in a rearrangement of the disordered areas into the porous network structure. During this rearrangement upon annealing, H-bonds are broken and newly formed until the thermodynamically stable phase, the porous network, is formed. It should be noted that annealing at temperatures >365 K did not result in the formation of another structure. Therefore, annealing can be used as an effective way to drive a self-assembled system into its thermodynamically most stable phase by making use of its error correction capability.

To obtain information on the structural relation of the porous network and the underlying graphene substrate, LEED measurements were performed at room temperature after annealing at 365 K. The LEED pattern of the porous network acquired at an energy of 70 eV is shown in Figure 5a. The ring-like diffraction pattern of graphene is marked by a red arrow, one of the first-order diffraction spots of the Cu(111) surface is indicated by a blue arrow and the diffraction pattern originating from the porous network is marked by a green arrow. The ring-like diffraction pattern for graphene exhibits intensity variations which suggest that certain graphene orientations with respect to the underlying Cu substrate are preferred. The diffraction pattern arising from the BTB honeycomb network is close to the (0,0) spot and consists of concentric rings each having six clear spots (Figure 5b). This indicates that similar to graphene the porous BTB network exhibits preferred orientations. Since the real space lattice parameters of the Cu(111) surface and graphene are known, the real space lattice parameter of the BTB network can be deduced, it amounts to 3.27 nm. This is in very good agreement with the lattice parameter obtained from STM. One of the principal Cu directions (blue dashed line in Figure 5b) and one of the unit cell directions of the porous network are parallel to each other. This can be inferred from the fact that a diffraction spot of the BTB network is located on

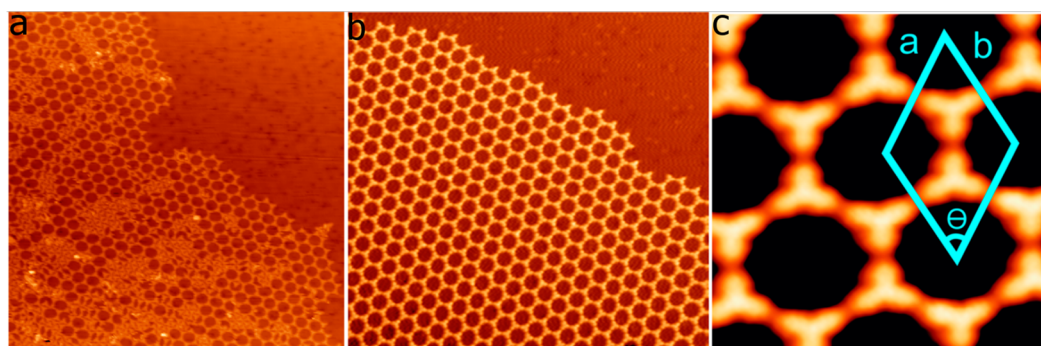


Figure 4. (a) STM image ($75.5 \text{ nm} \times 75.5 \text{ nm}$, $U = -2.1 \text{ V}$, $I = 10 \text{ pA}$) for BTB deposited onto graphene/Cu(111) held at room temperature. A porous network forms which exhibits several disordered areas. (b) STM image ($65 \text{ nm} \times 62 \text{ nm}$, $U = -1.5 \text{ V}$, $I = 10 \text{ pA}$) for submonolayer coverage of BTB on graphene/Cu(111) after annealing at 365 K. The quality of the porous network is highly improved. (c) High-resolution STM image ($7.7 \text{ nm} \times 7.7 \text{ nm}$, $U = -1.5 \text{ V}$, $I = 10 \text{ pA}$) of submonolayer coverage of BTB on graphene/Cu(111) showing submolecular resolution for the individual BTB molecules. The unit cell is drawn in blue.

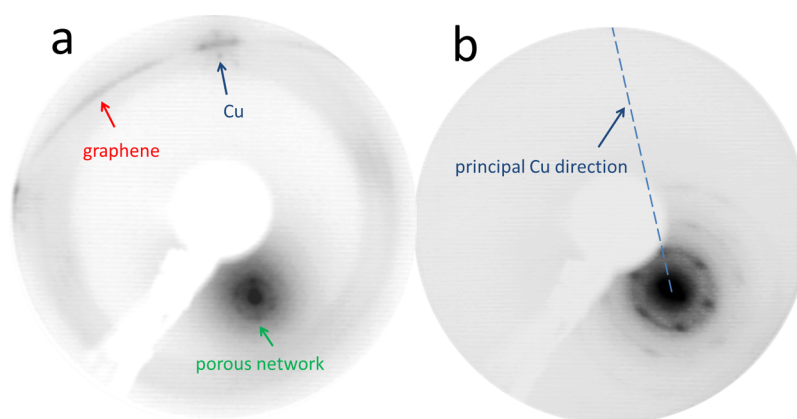


Figure 5. (a) LEED pattern (taken at a primary energy of 70 eV) of the porous BTB network on graphene/Cu(111) after annealing at 365 K. The features arising from the Cu surface, graphene and the BTB network are marked in blue, red and green, respectively. (b) LEED pattern for the same sample but taken at a primary energy of 16.6 eV. Now, the diffraction pattern arising from the porous BTB network can be seen more clearly.

the blue dashed line indicating a principal Cu direction. The diffraction pattern of graphene and the porous network have the ring-like diffraction pattern in common which, nevertheless, exhibits clear preferred directions. This suggests that the porous BTB network follows the orientation of graphene. On the other hand, if the porous BTB network would follow the orientation of the Cu(111) surface, the ring-like diffraction pattern present for the BTB network should not be observed.

Our study shows that the adsorption behavior of BTB on graphene is quite different from the adsorption behavior on Cu(111). On Cu(111), the BTB molecules get already partially deprotonated when deposited on a sample held at room temperature and thus, cannot form long-range ordered H-bonded networks-like the hexagonal porous network-based on double hydrogen bonding between the carboxylic acid end groups. Instead, the BTB molecules prefer to arrange in a close-packed structure. Upon annealing at elevated temperatures, all end groups can be deprotonated and the close-packed structure is exclusively formed. On the other hand, for deposition on graphene held at room temperature the porous network is the dominating assembly and only a few disordered patches are found. Upon moderate annealing, the porous network can be exclusively formed. This demonstrates that graphene can act as a buffer layer to (partially) decouple the molecules from the metallic substrate and to prevent the deprotonation. However, an influence from the metallic Cu substrate is still present. This

is the case because the BTB network aligns with regard to the graphene lattice which in turn aligns with regard to the principal Cu directions.

CONCLUSIONS

In summary, a comparative study on the molecular self-assembly of BTB on Cu(111) and graphene grown on Cu(111) was performed. On Cu(111) a partial deprotonation of the molecules was observed resulting in the coexistence of close-packed and porous structures at room temperature. Upon annealing, the carboxylic acid end groups are completely deprotonated and only the close-packed structure forms. In contrast, on graphene no deprotonation of the end groups takes place. Already when BTB is deposited onto graphene held at room temperature, the molecules primarily assembled in a porous network, but also disordered close-packed structures were found. With the help of moderate annealing, long-range ordered domains of the porous network can be exclusively fabricated. LEED measurements indicate that the orientation of the porous BTB network follows the graphene lattice which in turn exhibits preferred orientations with regard to the Cu(111) surface.

Our study shows that graphene can effectively serve as a decoupling layer for the formation of long-range ordered self-assembled molecular structures. On the one side the molecule substrate interaction is reduced (molecular chemisorption to

the metal is prevented which can hinder the formation of self-assembled structures) while on the other side the molecules still “feel” the metal underneath the graphene layer. This influence of the metal can be used to tune the molecular adsorption energy in dependence of the type of metal used and offers the possibility to let the molecules and the metal interact selectively.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05541.

Additional STM data of BTB on Cu(111) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: m.a.stohr@rug.nl (M.S.). Telephone: +31 50 363 4438.

Notes

The authors declare no competing financial interest.

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